

(10)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 074 253**  
**B1**

(12)

# EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 18.06.86

(51) Int. Cl.<sup>4</sup>: C 11 B 9/00, C 07 C 121/16

(21) Application number: 82304628.9

(22) Date of filing: 02.09.82

(54) Aliphatic nitriles.

(30) Priority: 03.09.81 GB 8126748

(43) Date of publication of application:  
16.03.83 Bulletin 83/11(45) Publication of the grant of the patent:  
18.06.86 Bulletin 86/25(84) Designated Contracting States:  
BE CH DE FR GB LI NL(58) References cited:  
US-A-2 912 455  
US-A-3 739 007

HELVETICA CHIMICA ACTA, vol. 61, fasc. 7, no.  
243, July 1978, pages 2560-2578; A. FISCHLI:  
"243. Cob(II)alamin als Katalysator 1.  
Mitteilung. Reduktion von gesättigten Nitrilen  
in wässriger Lösung"

IDEM

S. ARCTANDER: "Perfume and flavor  
chemicals", 1969, Montclair, N.Y., US;

(73) Proprietor: UNILEVER PLC  
Unilever House Blackfriars P.O. Box 68  
London EC4P 4BQ (GB)  
(84) GB

(73) Proprietor: UNILEVER NV  
Burgemeester s' Jacobplein 1 P.O. Box 760  
NL-3000 DK Rotterdam (NL)  
(84) BE CH DE FR LI NL

(72) Inventor: Sell, Charles Stanley  
Woodlands Smeeth  
Near Ashford Kent (GB)

(74) Representative: Farndon, John Ernest et al  
UNILEVER PLC Patents Division P.O. Box 68  
Unilever House  
London EC4P 4BQ (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Learnington Spa, England.

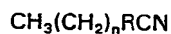
EP 0074 253 B1

## Description

This invention relates to substituted saturated aliphatic nitriles, more particularly to alpha- and beta-substituted nitriles which have been found to have value in perfume compositions.

Various substituted aliphatic nitriles have been known for some years, but hitherto their value as perfume components has not been appreciated. Our work has shown that certain of the alpha- and beta-substituted aliphatic nitriles, some of which are novel, have particular merit in perfumery compositions.

Accordingly, the present invention provides a perfume composition comprising perfume components and an organoleptically discernible amount of a nitrile of the formula:



in which

R=—CHCH<sub>3</sub>— or —CHCH<sub>3</sub>CH<sub>2</sub>— and in which, when R=—CHCH<sub>3</sub>—, n is an integer from 5—9 and when R=—CHCH<sub>3</sub>CH<sub>2</sub>—, n is an integer from 4—8.

In addition, this invention provides certain novel substituted nitriles of particular value in perfume formulations, having the formula:



in which n is 6, 7 or 8.

The nitriles useful in perfume compositions provided by this invention have, in addition to their useful odour characteristics, good stability when used in perfume formulations which are to be used or stored in an aggressive environment, such as in soaps, disinfectants, laundry powders and other compositions in which active chemicals are present or which have to withstand the effects of daylight or heat.

The nitriles useful according to this invention may be prepared by various processes, but a convenient process for the preparation of the alpha-substituted nitriles is as follows:

## Procedure A

A solution of the required methyl alkyl ketone (50 m mol) and tosylmethylisocyanide (12 g, 60 m mol) in dry, diglyme (120 ml) was added over 15 minutes at 0°C under nitrogen to a stirred solution of potassium t-butoxide (freshly prepared from potassium 4.3 g, 0.11 g atom) in dry t-butanol (100 ml) and diglyme (100 ml). When the addition was complete, the mixture was allowed to warm to room temperature then stirred for 2 hours and left to stand overnight. The resultant solution was poured into water (400 ml) and extracted with light petroleum (3×100 ml, bp 40—60°C). The combined organic extracts were washed with water (2×500 ml), then brine (500 ml) and dried (MgSO<sub>4</sub>). The solvent was removed under reduced pressure and the residue chromatographed using a column (3 cm diameter, 30 cm height) of silica gel with 5% ether in light petroleum (bp. 40—60°C) as solvent. Those fractions containing the product were freed of solvent under reduced pressure and the residue distilled to give the desired 2-methyl substituted nitrile.

A convenient process for the preparation of the beta-nitriles is as follows:

## Procedure B

The required methyl alkyl ketone (1 mol), cyanoacetic acid (93.5 g, 1.1 mol), ammonium acetate (13 g, 0.17 mol) and toluene (175 ml) were stirred under reflux (pot temperature 140—160°C) in a Dean-Stark apparatus until carbon dioxide ceased to be evolved (3—6 hours). The resultant mixture was cooled, washed with saturated aqueous sodium hydrogen carbonate (2×50 ml) and water (50 ml) then the solvent was removed under reduced pressure. The crude mixture of nitriles was then added to one quarter of its volume of 50% aqueous sodium hydroxide to which Tergitol\* (3 drops) had been added. The resulting mixture was stirred under reflux for 1 hour then cooled. The organic layer was removed, washed with water (3×50 ml) and distilled. 5% Palladium on carbon (0.1% by weight relative to the nitrile mixture) was then added followed by ethyl acetate (2×weight of distillate) and the suspension stirred vigorously in an atmosphere of hydrogen until uptake of gas ceased. The catalyst was removed by filtration and the solvent by evaporation under reduced pressure. Fractional distillation of the residue afforded the desired 3-methyl substituted nitrile.

The following table sets out the physical and the organoleptic properties of the nitriles useful in this invention:

\*Tergitol is a Registered Trade Mark for a surfactant (Union Carbide).

## 0 074 253

TABLE

	Sample	Series	Carbon chain length	Name
5	1	$\alpha$ -methyl	8	2-methyloctanonitrile
	2	$\alpha$ -methyl	9	2-methylnonanonitrile
10	3	$\alpha$ -methyl	10	2-methyldecanonitrile
	4	$\alpha$ -methyl	11	2-methylundecanonitrile
15	5	$\alpha$ -methyl	12	2-methyldodecanonitrile
	6	$\beta$ -methyl	8	3-methyloctanonitrile
	7	$\beta$ -methyl	9	3-methylnonanonitrile
20	8	$\beta$ -methyl	10	3-methyldecanonitrile
	9	$\beta$ -methyl	11	3-methylundecanonitrile
25	10	$\beta$ -methyl	12	3-methyldodecanonitrile

TABLE (contd.)

	Sample	Structure	Preparation
30	1	$\text{CH}_3(\text{CH}_2)_5\text{CHCH}_3\text{CN}$	Procedure A, 76% yield from 2-octanone
	2	$\text{CH}_3(\text{CH}_2)_6\text{CHCH}_3\text{CN}$	Procedure A, 69% yield from 2-nonanone
35	3	$\text{CH}_3(\text{CH}_2)_7\text{CHCH}_3\text{CN}$	Procedure A, 77% yield from 2-decanone
	4	$\text{CH}_3(\text{CH}_2)_8\text{CHCH}_3\text{CN}$	Procedure A, 74% yield from 2-undecanone
40	5	$\text{CH}_3(\text{CH}_2)_9\text{CHCH}_3\text{CN}$	Procedure A, 59% yield from 2-dodecanone
45	6	$\text{CH}_3(\text{CH}_2)_4\text{CHCH}_3\text{CH}_2\text{CN}$	Procedure B, 59% yield from 2-heptanone
	7	$\text{CH}_3(\text{CH}_2)_5\text{CHCH}_3\text{CH}_2\text{CN}$	Procedure B, 16% yield from 2-octanone
50	8	$\text{CH}_3(\text{CH}_2)_6\text{CHCH}_3\text{CH}_2\text{CN}$	Procedure B, 49% yield from 2-nonanone
	9	$\text{CH}_3(\text{CH}_2)_7\text{CHCH}_3\text{CH}_2\text{CN}$	Procedure B, 35% yield from 2-decanone
55	10	$\text{CH}_3(\text{CH}_2)_8\text{CHCH}_3\text{CH}_2\text{CN}$	Procedure B, 26% yield from 2-undecanone

# 0 074 253

TABLE (contd.)

	Sample	Boiling point (lit. bp)	Odour description
5	1	78—80°C at 8 m bar (85 at 10 mm Hg)	Floral jasminic character with some celery aspects and a hint of coconut/lactone— very diffusive.
10	2	72—73°C at 3 m bar (100 at 10 mm Hg)	Soft, floral, lactonic, jasmine/peachy character.
15	3	85—87°C at 3 m bar (115 at 10 mm Hg)	A fine, light, jasmine/floral character with a soft peach quality.
20	4	84°C at 1 m bar (133 at 12 mm Hg)	Fresh, floral with some lilac character—tenaceous.
25	5	125—127°C at 7 m bar (146 at 10 mm Hg)	Soft, floral with a green jasminic type odour—very persistent.
30	6	66—68°C at 4 m bar (207—8 at 760 mm Hg)	An unusual floral type consisting of a distinct fatty jasminic character combined with an agrumen quality.
35	7	93°C at 8 m bar (95—6 at 2—3 mm Hg)	Fresh, jasminic floral type with a slightly green quality.
40	8	72—74°C at 0.7 m bar	Soft, citrus floral— reminescent of jasmine.
45	9	99—100°C at 3 m bar	Light, fresh, green, floral suggesting lilac, with slight citrus undertones.
50	10	95—97°C at 0.7 m bar	Distinct orange character which is suffused by a light green sea-fresh quality.

The following are two examples of perfume compositions comprising the nitriles of this invention:

# 0 074 253

## Formula 1

	Phenylethyl Alcohol	30.5
	Terpineol	6.0
5	Paratertiary butyl cyclohexyl acetate high cis (PPL)	15.0
	Benzyl Salicylate	14.8
10	Cinnamic Alcohol	10.0
	Sandalone® (PPL)	5.0
	Galaxolide® (IFF)	3.0
15	Hexyl Cinnamic Aldehyde	10.0
	Coumarin	2.0
20	Rose Base AB 380 (PPL)	2.0
	Isoeugenol	0.1
	Vetivert Brazilian	0.1
25	Nitrile No. 3	1.5

Formula 1 in the absence of nitrile 3 has a floral, woody bouquet suitable for a toilet soap. The addition of 1.5% of nitrile 3 enhances the overall freshness, giving a light floral, fruity effect. Using the above formulation but substituting nitrile 9 in place of nitrile 3, a perfume is created having an added fresh lightness with an enhanced floral, fruity and citrus character.

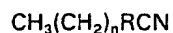
The three novel nitriles provided by this invention are those numbered 8, 9 and 10 in the samples list and their mass spectral data are as follows.

35	Sample		Base peak	M1	M2	M3	M4	M5
	8	C <sub>10</sub>	41	43:85	57:84	68:66	55:50	96:46
	9	C <sub>11</sub>	41	57:85	43:84	68:56	55:50	69:43
40	10	C <sub>12</sub>	41	57:92	43:90	55:54	68:53	70:48

Perfumes formulated using as an odorous component the nitriles provided by this invention may be employed in the various products, such as soaps, detergents, hairsprays, talcum powders and the like, which are normally augmented by the addition of a perfume.

## Claims

1. A perfume composition comprising perfume components characterized in that it further contains an organoleptically discernible amount of a nitrile of the formula:

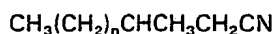


in which

R=—CHCH<sub>3</sub>— or —CHCH<sub>3</sub>CH<sub>2</sub>— and in which, when  
R=—CHCH<sub>3</sub>—, n is an integer from 5—9 and when  
R=—CHCH<sub>3</sub>CH<sub>2</sub>—, n is an integer from 4—8.

2. A perfume composition as claimed in claim 1 in which the amount of the nitrile does not exceed 95% by weight of the perfume composition.

3. A substituted nitrile having the formula:

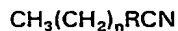


in which n is 6, 7 or 8.

4. A product comprising a perfume composition as claimed in claim 1 or claim 2.

# **Patentansprüche**

1. Parfümzusammensetzung mit Parfümbestandteilen, dadurch gekennzeichnet, daß sie außerdem eine organoleptisch wahrnehmbare Menge eines Nitrils der Formel



enthält, in der

R=—CHCH<sub>3</sub>— oder —CHCH<sub>3</sub>CH<sub>2</sub>— ist und in der bei

R=—CHCH<sub>3</sub>— n eine ganze Zahl von 5 bis 9 und bei

R=—CHCH<sub>3</sub>CH<sub>2</sub>— n eine ganze Zahl von 4 bis 8 ist.

2. Parfümzusammensetzung nach Anspruch 1, in der die Menge des Nitrils 95 Gew.-% der Parfümzusammensetzung nicht überschreitet.

3. Substituiertes Nitril der Formel:

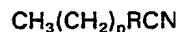


in der n 6, 7 oder 8 ist.

4. Produkt mit einem Gehalt an einer Parfümzusammensetzung nach Anspruch 1 oder 2.

## **Revendications**

1. Composition de parfum comprenant des composants de parfum, caractérisée en ce qu'elle contient en outre une quantité organoleptiquement discernable d'un nitrile de formule:



où

R=—CHCH<sub>3</sub>— ou —CHCH<sub>3</sub>CH<sub>2</sub>— et où, lorsque

R=—CHCH<sub>3</sub>—, n est un nombre entier allant de 5 à 9 et lorsque

R=—CHCH<sub>3</sub>CH<sub>2</sub>—, n est un nombre entier allant de 4 à 8.

2. Composition de parfum selon la revendication 1 où la quantité de nitrile n'excède pas 95% en poids de la composition de parfum.

3. Nitrile substitué ayant la formule:



où n vaut 6, 7 ou 8.

4. Produit comprenant une composition de parfum telle que revendiquée dans les revendications 1 ou